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March 24, 1993

Dr. James Butler
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Subject: Quarterly Scientific Report Contract #N00014-93-K-2021

Dear Dr. Butler:

This letter is intended to serve as the quarterly technical report for the project "Optical Diagnostics of Diamond CVD in DC Arc-Jets," #N00014-93-K-2021 for the period October 16, 1992 through February 15, 1993. During the first three months of this project collaborations have been initiated with Norton Diamond Films and with Professor Mark Cappelli of the High Temperature Gas Dynamics Laboratory at Stanford.

Dr. Jay B. Jeffries, the Principle Investigator, visited Dr. Richard Woodin of Norton Diamond Films at the Technion facility in Irvine, California on October 26, 1993. Norton's optical diagnostics laboratory was toured and the difficulties of laser-based diagnostics in an industrial environment were considered in detail. During this visit, Norton's plans to observe plasma emission discussed, and the influence of the excitation mechanism which produces the molecular excited states was elucidated. The molecular emission in a chemically reacting plasma can arise from three different excitation mechanisms: thermal emission, electron impact excitation, and chemiluminescent reaction. Each of these excitation mechanisms produces a distinctly different population distribution in the rotational and vibrational levels of the electronically excited state. Each of these mechanisms is briefly discussed here.

Thermal excitation produces a rotational and vibrational distribution which is described by a single Boltzmann temperature, and all the electronic excited state populations of the various chemical species are similarly described by the same Boltzmann distribution. The emission intensity relies only on the excitation energy of the emitting state and molefraction for a particular chemical species. Collisional quenching does not play a role for thermal excitation because the system is in steady state and any population collisionally removed is simultaneously collisionally repopulated.

Electron impact excitation produces a total excited state population which depends on the convolution of the electron energy distribution with the excitation cross section. Thus, the emission intensity is most sensitive to the molefraction for the particular chemical species and the electron energy. The vibrational distribution in the excited state is determined by the Franck-Condon principle; the intranuclear separation of the molecule does not change during electron impact excitation similarly, the angular momentum of the molecule is not altered during the excitation process, and the rotational distribution reflects the thermal distribution of the ground state molecules.

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Thus, the signature for electron impact excitation is a Franck-Condon vibrational distribution and a thermal rotational distribution. The rotational distribution can be used to provide a gas temperature, once the electron-impact excitation mechanism is established.

Chemiluminescent reactions produce an excited state vibrational and rotational distribution which is in general far from that described by the gas temperature. Although chemiluminescent reactions are not required to produce a thermal product distribution, the reactions which proceed through a bound intermediate do produce a thermal product distribution; however, the distribution reflects the total energy of the system including the energy released in the reaction in addition to the gas temperature. This extra energy can produce rotational and vibrational distributions far from the gas temperature. Rotational and vibrational energy transfer collisions drive this initial distribution towards the gas temperature; however, collisional quenching collisions remove the population from the emitting excited state and compete with the thermalization. Thus, most of the emission is produced from excited molecules which have not completely thermalized producing an emission distribution which is hotter than the gas temperature. This phenomena is well known for flame emission from OH, CH, and C_2, and has been observed at SRI in 200 Torr diamond depositing arc-jet plasmas.

The plasma emission spectrum from the Norton plasma has subtle differences with the SRI spectrum. Careful analysis of the CH A-X and CH B-X, show that the vibrational distribution appears to be consistent with Franck-Condon excitation of the CH X state. Thus, the emission in the Norton jet appears to be produced by electron impact emission. During November and December, daily fax, e-mail, and phone conversations led to a collaboration between SRI and Norton which focused on understanding the CH emission. SRI fit the rotational envelope of the CH A-X 0,0 emission with a 2500 K distribution as shown in Fig. 1. SRI then provided their spectral simulation program to Norton, with permission from Richard N. Zare who originally wrote the simulation code. Norton altered the code to run on their laboratory computers and has integrated this code with their process control research effort.

In addition to collaborating with Norton on the CH emission mechanism, SRI was able to identify other features in the emission spectrum from the Norton arc-jet. Thus, the Norton-SRI collaboration during the first quarter of the contract has been incredibly successful.

The SRI plans for laboratory work have been altered as a result of the Norton collaboration. The SRI arc-jet at 200 Torr has significantly different process conditions and has a different emission spectrum. Thus, we decided to assemble a diamond depositing jet which operates in pressure and gas velocity regimes closer to the Norton conditions. Instead of beginning this development effort from scratch, SRI has begun a collaboration with Professor Mark Cappelli at Stanford University. Using the NRL funds we have provided the student stipend to one of his students, Mr. Doug Beattie, and he has worked with Dr. Mike Brown, an SRI postdoctoral fellow, to install a Cappelli arc-jet into an SRI vacuum chamber with optical access and sufficient translation to map the entire plume both on and off axis. This collaboration has just begun at the end of the first three month period of the contract.

I will be happy to address any technical questions on the work described in this letter or work proposed in the contract. Feel free to contact me at (415) 859 5341 phone, (415) 859 6196 fax, and Jeffries@MPLVAX.SRI.COM e-mail.

Sincerely,

Jay B. Jeffries
Molecular Physics Laboratory

JBJ/adw

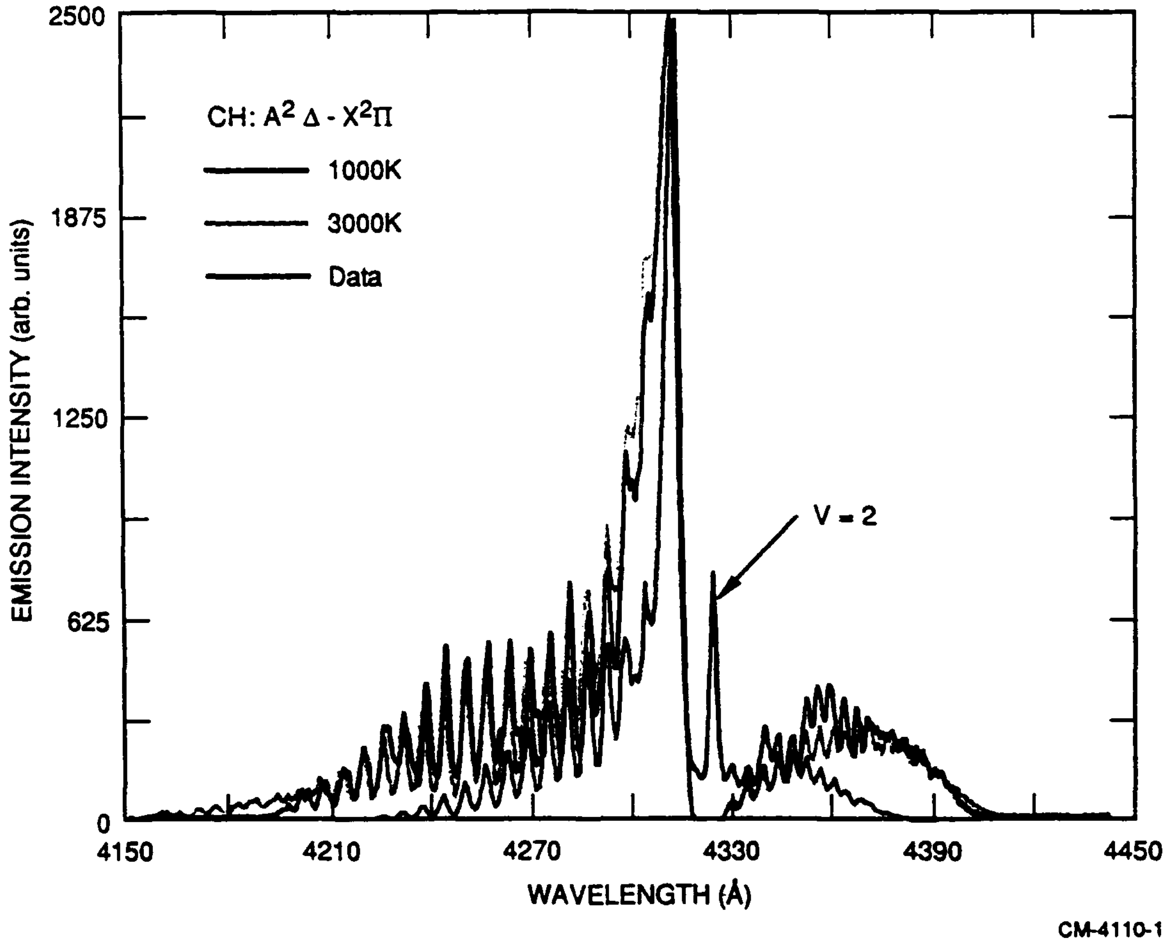

Figure 1. CH A-X emission spectrum from Norton dc-arc-jet plasma.